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A THERMODYNAMIC ANALYSIS OF SOLUBILITY
IN LIQUID METAL SYSTEMS

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ABSTRACT

Binary liquid-metal solubility equilibria of the type A (in solid or liquid phase) \rightleftharpoons A (in liquid B) are analyzed in terms of the fundamental thermodynamic solution parameters $\Delta\bar{H}_{A(l)}^\infty$ and $\Delta\bar{S}_{A(l)}^{xs\infty}$, the heat and entropy, respectively, of solution of the liquid solute at infinite dilution in the liquid solvent. A general method for the treatment of equilibrium solubility data is developed and is termed the Σ' -function method, in view of its similarity to the standard Σ -function method for the treatment of vapor-pressure data. By the assumption of subregular behavior of the liquid metal solution, the Σ' -function method is applicable to moderately concentrated solutions. Consideration is given to details of the application of the method to the three general states of the solute phase: (a) pure solute A, (b) terminal solution of B in A, and (c) intermetallic compound A_xB_{1-x} . The Σ' -function method is applied to five binary systems for which data are available in the literature: Mg-Fe, Pb-Ni, Bi-Be, Pb-Zn, and Pb-Cu. The results are in close agreement with the results published in the literature.

PROBLEM STATUS

This report concludes one phase of the problem. Work on other phases is continuing.

AUTHORIZATION

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A THERMODYNAMIC ANALYSIS OF SOLUBILITY IN LIQUID METALS

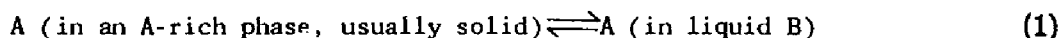
INTRODUCTION

A major problem in the efficient utilization of nuclear energy is the extraction of heat from a reactor operating at a high temperature. The properties of many liquid metals recommend their use as heat transfer fluids, but a serious obstacle to their application lies in the phenomenon of mass transfer (1). In general, a liquid metal circulating in a heat exchanger tends to dissolve the container metal in the hot zone and to transfer this metal to a cooler zone where it may deposit and plug the conduit. In recent studies (2,3) attention has been directed to the fundamental thermodynamic condition for mass transfer, namely, that the solubility of the solid container metal in the liquid metal must vary with temperature. Although kinetic factors, such as diffusivities and rates of dissolution, nucleation, and growth, play important roles in determining the rate of mass transfer, it is recognized that the basic driving force for the process lies in the variation of solubility with temperature.

In previous studies of solubility data for liquid metal systems (2,3) it was observed that the temperature coefficients of solubility of solid metals in dilute liquid metal solutions correlate well with the disparities in sizes of the solvent and solute atoms. This correlation is shown in Fig. 1. The temperature coefficients are expressed in the form $-d(R \ln N_{A(\ell)})/d(1/T)$, where $N_{A(\ell)}$ is the atom fraction of the solute A in the saturated liquid metal B, R is the gas constant, and T is the Kelvin temperature. In a recent communication (3), the thermodynamic basis for this form of the temperature coefficient was briefly outlined, and some structural implications of the correlation with the atomic size factor were discussed.

The purpose of the present report is to examine more rigorously the solubility relations for binary metal systems and to present a method for the treatment of solubility results in terms of the basic thermodynamic parameters of the systems.

The term solubility as used herein refers to the equilibrium



where the extent of solution of A in liquid B is determined by the equivalence of the chemical potentials of each component in the two phases. Two important thermodynamic properties of the liquid solution, which can be evaluated from measurements of such equilibria, are the energy and entropy changes accompanying the transfer of a solute atom from pure liquid solute to pure liquid solvent. These quantities are expressed here by the partial molal enthalpy $\Delta \bar{H}_{A(\ell)}^\circ$ and the partial molal excess entropy $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$ of

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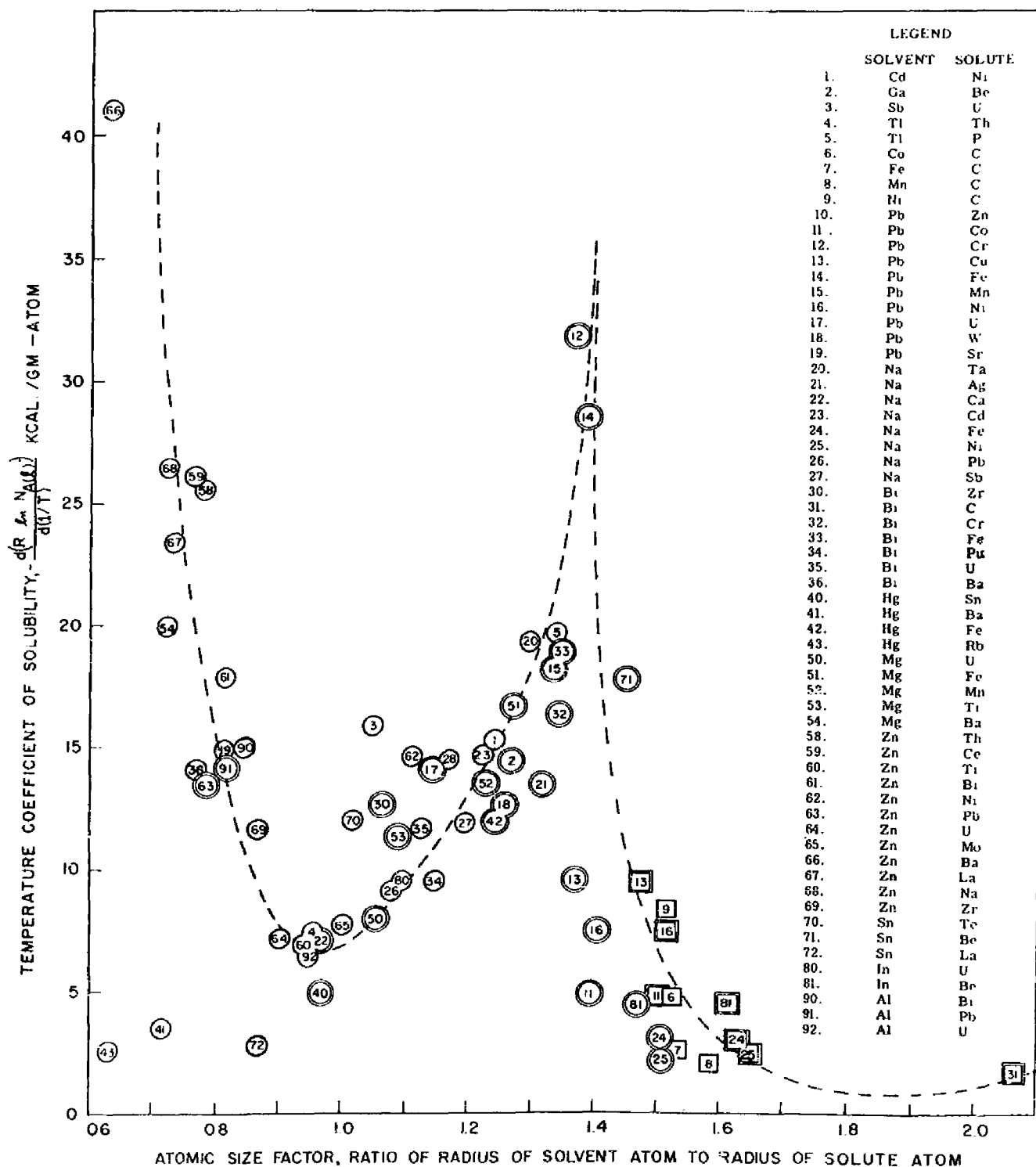


Fig. 1 - Temperature coefficients of solubility in binary metallic systems as a function of size factor. Double symbols (\odot or \square) refer to systems in which the solute-rich phase is essentially pure solute.

component A at infinite dilution in liquid B.* The method developed below for the treatment of solubility data in terms of $\Delta\bar{H}_{A(l)}^{\infty}$ and $\Delta\bar{S}_{A(l)}^{xs,\infty}$ will be termed the Σ -function method owing to its similarity to one of the standard methods for the treatment of vapor pressure data (4). The similarity results from the fact that in both cases the process is one of the transfer of an atom from a condensed phase to an attenuated phase, viz., a gas in the case of vaporization and a dilute solution in the case of solubility. The Σ -function method is directly applicable to dilute solutions and, by means of approximations based on the subregular solution model (5),[†] may be extended to treat moderately concentrated solutions.

From the viewpoint of a further understanding of alloying behavior (in solid as well as liquid alloys), measurements of solubility are valuable for two reasons. First, values of $\Delta\bar{H}_A^{\infty}$ and $\Delta\bar{S}_A^{xs,\infty}$ can be determined for systems whose ranges of composition are so low that ordinary thermodynamic methods for their measurement are impractical. Second, systems of low solubility are of considerable theoretical interest in studying the effect of the atomic size factor since these systems commonly have size effects so large as to overshadow other possible effects (3). Solubility data for liquid metals appear abundantly in the literature, but in only a relatively few cases (e.g., Kleppa (7,8)) have the data been treated to evaluate $\Delta\bar{H}_{A(l)}^{\infty}$ and $\Delta\bar{S}_{A(l)}^{xs,\infty}$ and their corresponding uncertainties.

DEVELOPMENT OF THE GENERAL SOLUBILITY RELATION

The approach is to relate the properties of the solute A dissolved in liquid B to the properties of pure A in the liquid state. In most cases this reference state of the pure liquid solute is hypothetical, at the temperatures of interest, and the properties of the pure liquid must be defined by a reasonable and continuous extrapolation of the properties above the melting point.

The general solubility relation is developed from consideration of the reaction scheme shown in Fig. 2 for component A of the system A-B. The symbols A(s) and A(l) refer to the pure component A in the solid and liquid states, respectively. $N_{A(s)}$ and $N_{A(l)}$ are the concentrations of component A in the two mutually saturated phases. The various terms in ΔF represent the free-energy changes involved in the transfer of one mole of component A from one phase or state to another, e.g., ΔF_A^m is the free energy of melting pure A at the temperature of the solubility equilibrium.

*The partial molal excess quantities represent deviations from the properties of ideal solutions; thus,

$$\Delta\bar{S}_{A(l)}^{xs} = \Delta\bar{S}_{A(l)} - \Delta\bar{S}_{A(l)}^{\text{ideal}} = \Delta\bar{S}_{A(l)} + R \ln N_{A(l)}, \quad (2)$$

and

$$\Delta\bar{F}_{A(l)}^{xs} = \Delta\bar{F}_{A(l)} - \Delta\bar{F}_{A(l)}^{\text{ideal}} = \Delta\bar{F}_{A(l)} - RT \ln N_{A(l)}, \quad (3)$$

where $\Delta\bar{F}_{A(l)}^{xs}$ is the partial molal excess free energy. From these definitions it should be noted that

$$\Delta\bar{H}_{A(l)}^{xs} = \Delta\bar{H}_{A(l)}. \quad (4)$$

[†]The subregular solution model, whose name was proposed by Hardy (6), differs from the well-known regular solution model in that several additional parameters are available to provide for the deviation of real solutions from regular behavior.

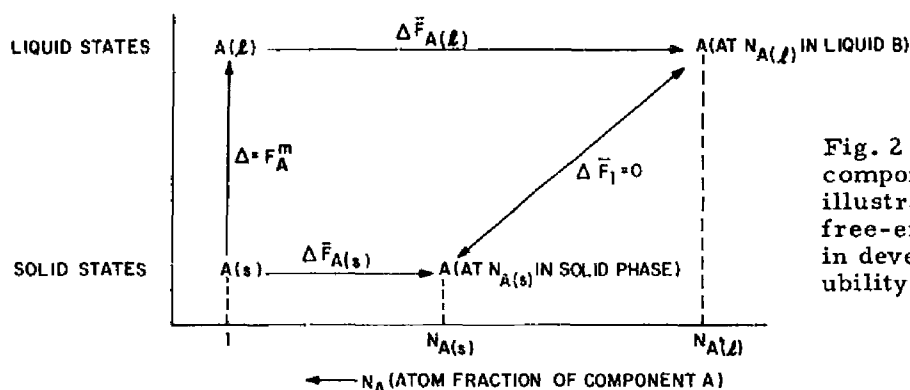


Fig. 2 - Reaction scheme for component A of a system A-B, illustrating the states and free-energy changes employed in developing the general solubility relation

The solid and liquid phases are at equilibrium with each other; therefore $\Delta \bar{F}_1 = 0$, and (see Fig. 2)

$$\Delta \bar{F}_{A(l)} + \Delta F_A^m = \Delta \bar{F}_{A(s)} \quad (5)$$

Since the thermodynamic properties of the liquid binary solution are determined by $\Delta \bar{F}_{A(l)}$ and its variation with temperature, the procedure is to evaluate each free-energy change in Eq. (5) in terms of $N_{A(l)}$, $N_{A(s)}$, $\Delta \bar{F}_{A(l)}$, $\Delta \bar{S}_{A(l)}$, and the other relevant thermodynamic properties of the system A-B.

The free energy of melting of pure A, ΔF_A^m , can be obtained by integration of

$$\frac{d\Delta F_A^m}{dT} = -\Delta S_A^m \quad (6)$$

where ΔS_A^m is the entropy of melting of pure A at temperature T. ΔS_A^m is given by

$$\Delta S_A^m = \Delta S_{A, T_A^m}^m + \int_{T_A^m}^T \left(\frac{\Delta C_{p, A}^m}{T} dT \right) \quad (7)$$

where T_A^m is the melting point of pure A and $\Delta C_{p, A}^m$ is the difference in heat capacities of liquid and solid A. Integrating Eq. (6) and making use of the fact that $\Delta F_{A, T_A^m}^m = 0$

$$\Delta F_A^m = \Delta S_{A, T_A^m}^m (T_A^m - T) - \int_{T_A^m}^T \int_{T_A^m}^T \left(\frac{\Delta C_{p, A}^m}{T} dT \right) dT \quad (8)$$

However, if component A undergoes transitions in the solid state or if $\Delta C_{p, A}^m$ cannot be represented by a simple analytic function, the integral in Eq. (8) becomes cumbersome to evaluate and it is more satisfactory to make use of the free-energy functions to evaluate ΔF_A^m . The free-energy function, f_{ef} , is defined (9) by

$$f_{ef} = \left(\frac{F_T - H_{st}}{T} \right) = \left(\frac{H_T - H_{st}}{T} \right) - S_T \quad (9)$$

where T is the Kelvin temperature, st refers to the standard state at a specified standard temperature (usually 298.15°K), and S_T is the absolute entropy at T°K. The free-energy functions are readily constructed for the solid and liquid over their respective temperature ranges of stability by evaluating the terms on the right-hand side of Eq. (9)

from standard tables (9 to 14). An important practical characteristic of the free-energy function is that it varies relatively slowly with temperature, so that a plot of the free-energy function as a function of temperature for the condensed phases of a material can be readily constructed from a relatively small number of points.

The construction of the free-energy function for the liquid at temperatures below the melting point is usually accomplished by assuming that a simple heat capacity expression, e.g.,

$$C_{p,A(\ell)} = a + bT, \quad (10)$$

is representative of the liquid properties below, as well as above, the melting point. If Eq. (10) is used, the free-energy function of pure liquid A is then given by

$$\begin{aligned} \left(\frac{F_T - H_{st}}{T} \right)_{A(\ell)} &= \left(\frac{H_{T_A^m} - H_{st}}{T} \right)_{A(\ell)} - S_{T_A^m, A(\ell)} + a + bT_A^m \\ &\quad - \frac{T_A^m}{T} \left(a + \frac{b}{2} T_A^m \right) - a \ln \left(\frac{T}{T_A^m} \right) - \frac{b}{2} T \end{aligned} \quad (11)$$

where

$$(H_{T_A^m} - H_{st})_{A(\ell)} \text{ and } S_{T_A^m, A(\ell)}$$

are the enthalpy (relative to the standard temperature st) and the absolute entropy of the pure liquid A at its melting point. Since the free-energy functions for solid and liquid A both relate to the same standard state of pure A at the standard temperature st , the free energy of melting is given by

$$\Delta F_A^m = T \left[\left(\frac{F_T - H_{st}}{T} \right)_{A(\ell)} - \left(\frac{F_T - H_{st}}{T} \right)_{A(s)} \right]. \quad (12)$$

The term $\Delta \bar{F}_{A(s)}$ of Eq. (5) provides for the fact that the activity of A in the phase in equilibrium with the liquid solution may be lower than that of pure A. Formally, this term is given by

$$\Delta \bar{F}_{A(s)} = RT \ln a_{A(s)} = RT \ln (\gamma_{A(s)} N_{A(s)}) \quad (13)$$

where $a_{A(s)}$, $\gamma_{A(s)}$, and $N_{A(s)}$ are the activity, activity coefficient, and atom-fraction of component A in the solid phase, respectively. $\Delta \bar{F}_{A(s)}$ may be evaluated exactly if activities and phase boundaries have been well determined for the solid phase; if these data are not available, resort must be made to the approximations to be treated later.

The term $\Delta \bar{F}_{A(\ell)}$ of Eq. (5) may be written as

$$\Delta \bar{F}_{A(\ell)} = \Delta \bar{H}_{A(\ell)} - T \Delta \bar{S}_{A(\ell)}; \quad (14)$$

$$\Delta \bar{F}_{A(\ell)} = \Delta \bar{H}_{A(\ell)} + RT \ln N_{A(\ell)} - T \Delta \bar{S}_{A(\ell)}^{xs}. \quad (15)$$

$\Delta \bar{S}_{A(\ell)}^{xs}$ represents the deviation from the ideal entropy of mixing calculated on a substitutional basis and may consist of thermal (i.e., vibrational) as well as configurational contributions. $\Delta \bar{H}_{A(\ell)}$ represents the energy difference between A atoms in the liquid B solution and A atoms entirely surrounded by A-neighbors, as in pure liquid A.

The general solubility relation is obtained by combining Eqs. (5), (13), and (15); thus,

$$\Delta \bar{H}_{A(\ell)} + RT \ln N_{A(\ell)} - T \Delta \bar{S}_{A(\ell)}^{xs} + \Delta F_A^m = RT \ln a_{A(s)} \quad (16)$$

Regrouping and dividing by T ,

$$R \ln N_{A(\ell)} + \frac{\Delta F_A^m}{T} - R \ln a_{A(s)} = -\frac{\Delta \bar{H}_{A(\ell)}}{T} + \Delta \bar{S}_{A(\ell)}^{xs} \quad (17)$$

In this form the solubility relation is suitable for application to the several types of solubility equilibria. For convenience, let the left-hand side of Eq. (17) be designated as the Σ -function, i.e.,

$$\Sigma = R \ln N_{A(\ell)} + \frac{\Delta F_A^m - \Delta \bar{F}_{A(s)}}{T} = R \ln \left(\frac{N_{A(\ell)}}{a_{A(s)}} \right) + \frac{\Delta F_A^m}{T} \quad (18)$$

In general, $\Delta \bar{H}_{A(\ell)}$ and $\Delta \bar{S}_{A(\ell)}^{xs}$ are functions of temperature and composition, but for very dilute solutions, e.g., $N_{A(\ell)} < 0.005$, the composition dependence may be neglected. Thus, if the values of Σ calculated from experimental results by Eq. (18) are plotted against the reciprocal of the Kelvin temperature, the slope of the tangent to the resulting curve is $-\Delta \bar{H}_{A(\ell)}^\infty$ and the intercept of the tangent at $1/T = 0$ is $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$. Since $\Delta \bar{H}_{A(\ell)}^\infty$ may be a function of temperature, the Σ values will generally define a gentle curve rather than a straight line. However, in actual cases, strong deviations from the Kopp-Neumann rule for the additivity of heat capacities are not expected for liquid alloys, and, in view of the scatter to be expected in experimental results for the solubilities, a straight line usually offers the most satisfactory fit.

In many binary metal systems the eutectic occurs at solute concentrations greater than $N_{A(\ell)} = 0.005$, and it is most desirable to extend the Σ -function method to treat these more concentrated solutions. Lumsden's extension of the regular solution model (15), termed the subregular solution model (5,6), has been found to give a good representation of the thermodynamic properties of many binary liquid systems (10) and offers a convenient method of introducing a first approximation for the concentration dependence of $\Delta \bar{H}_{A(\ell)}$ and $\Delta \bar{S}_{A(\ell)}^{xs}$. Thus, let

$$\Delta \bar{H}_{A(\ell)} = \Delta \bar{H}_{A(\ell)}^\infty N_{B(\ell)}^2 = \Delta \bar{H}_{A(\ell)}^\infty (1 - N_{A(\ell)})^2 \quad (19)$$

and

$$\Delta \bar{S}_{A(\ell)}^{xs} = \Delta \bar{S}_{A(\ell)}^{xs, \infty} N_{B(\ell)}^2 = \Delta \bar{S}_{A(\ell)}^{xs, \infty} (1 - N_{A(\ell)})^2 \quad (20)$$

Substituting in Eq. (17),

$$\Sigma' = \frac{\Sigma}{(1 - N_{A(\ell)})^2} = -\frac{\Delta \bar{H}_{A(\ell)}^\infty}{T} + \Delta \bar{S}_{A(\ell)}^{xs, \infty} \quad (21)$$

Values of Σ' calculated from experimental results for more concentrated solutions may now be plotted against $1/T$, and $\Delta \bar{H}_{A(\ell)}^\infty$ and $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$ are obtained from the slope of the resulting curve and its intercept at $1/T = 0$. Although the precision of this treatment for moderately concentrated solutions depends on how closely a given liquid alloy conforms to the subregular behavior postulated by Eqs. (19) and (20), the method appears to be frequently applicable to concentrations as high as $N_{A(\ell)} = 0.1$, which includes most systems of interest to current studies.

APPLICATION OF THE Σ -FUNCTION METHOD TO THREE GENERAL CASES

In calculating the Σ -function by Eq. (18), data are frequently not available to evaluate the term $\Delta \bar{F}_{A(s)} = RT \ln a_{A(s)}$, and approximations are then necessary in applying the Σ -function method. Thus, it is convenient to distinguish three types of solubility equilibria according to the nature of the phase in equilibrium with the liquid solution. The cases illustrated in Fig. 3 are: I, the A-rich phase has negligible solubility for B; II, the A-rich phase is a terminal solid or liquid solution showing appreciable solubility for B; III, the A-rich phase is an intermetallic compound.

It should be noted that a distinction between solid and liquid A-rich phases is unnecessary. If the A-rich phase is a liquid, then $\Delta F_A^m = 0$ in the calculation of the Σ -function. If the free-energy-function method is employed to evaluate ΔF_A^m , the phase transitions in A are properly accounted for in the calculation of ΔF_A^m , and all solubility data may be treated in one plot, irrespective of the number of transformations or reactions of the A-rich phase over the temperature range of the solubility data.

Case I

If the A-rich phase shows a maximum solubility for B of two atomic percent, or less, the contribution of $\Delta \bar{F}_{A(s)}$ to Σ will generally be less than one percent. Except for the most precise solubility data, $\Delta \bar{F}_{A(s)}$ may then be neglected, and the Σ -function becomes

$$\Sigma = R \ln N_{A(l)} + \frac{\Delta F_A^m}{T} \quad (22)$$

Case II

In cases of appreciable solubility of component B in the A-rich terminal solution it is frequently found that the phase boundaries in equilibrium with the liquid solution are

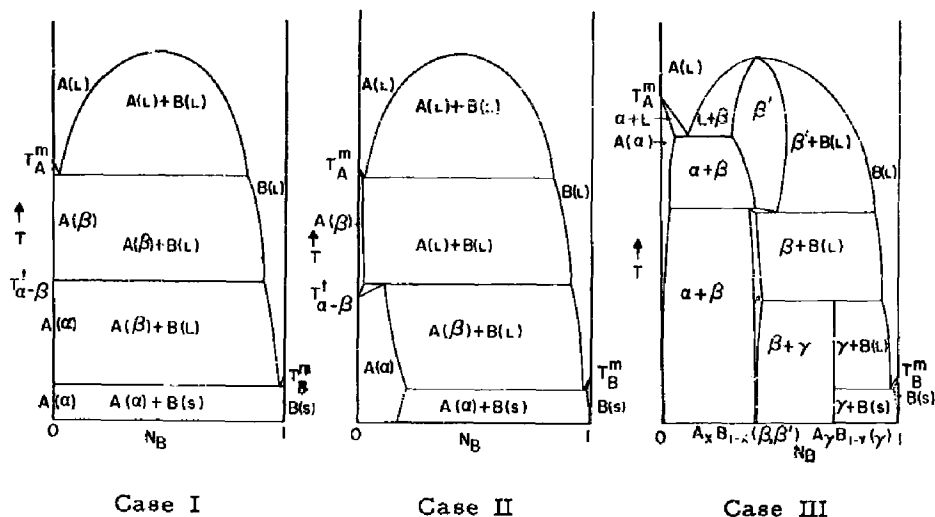


Fig. 3 - Three cases of liquid metal solubility equilibria distinguished according to the type of approximation employed in evaluating the activity of the solute A in the A-rich phase

at least approximately known but that the thermodynamic data necessary to evaluate $\gamma_{A(s)}$ are not available. Except in cases of unusually high solubility (i.e., $N_{A(s)} > 0.1$), it is reasonable to evaluate $\Delta\bar{F}_{A(s)}$ by the assumption of Raoult's law; thus, $\gamma_{A(s)} = 1$ and

$$\Sigma = R \ln \left(\frac{N_{A(l)}}{N_{A(s)}} \right) + \frac{\Delta F_A^m}{T}. \quad (23)$$

Case III

For systems in which the liquid solution is in equilibrium with an intermetallic phase, the thermodynamic information necessary for an exact evaluation of $\Delta\bar{F}_{A(s)}$ will only infrequently be available. In the relatively rare cases where the composition range of the intermetallic phase is very broad, e.g., the phase β' in Case III of Fig. 3, such thermodynamic data are indispensable for an evaluation of the liquid solubility in terms of $\Delta\bar{H}_{A(l)}$ and $\Delta\bar{S}_{A(l)}^{x_s, \infty}$. However, in most cases, the intermetallic phase is an ordered compound of very limited composition range, and $\Delta\bar{F}_{A(s)}$ may be approximated if the free-energy function for the intermetallic compound is known.

For the formation of an intermetallic compound A_xB_{1-x} from the pure components,



$$\Delta fef(A_xB_{1-x}) = fef_{A_xB_{1-x}} - [x fef_A + (1-x) fef_B]. \quad (25)$$

The free energy of formation of A_xB_{1-x} is given by

$$\frac{\Delta F^f(A_xB_{1-x})}{T} = \frac{\Delta H_{st}(A_xB_{1-x})}{T} + \Delta fef(A_xB_{1-x}). \quad (26)$$

If the free-energy functions for A, B, and A_xB_{1-x} are known, and if the standard heat of formation of A_xB_{1-x} has been measured, then $\Delta F^f(A_xB_{1-x})$ can be calculated for any temperature.

The method of estimating $\Delta\bar{F}_{A(s)}$ from $\Delta F^f(A_xB_{1-x})$ is indicated in Fig. 4. The partial molar free energy of component A in the intermetallic compound in equilibrium with the liquid solution is given by the intercept on the axis $N_A = 1$ of the tangent common to the free-energy curves of the intermetallic compound and the liquid solution. In cases of limited solubility, the free-energy curve of the liquid solution must turn sharply upward within the first few atom percent of solute concentration. Thus, only a second-order error is introduced by placing the tangent line through the origin rather than tangent to the as-yet-unknown curve for the liquid solution. The magnitude of the error will depend on the shape and position of both free-energy curves; however, it is clear that the error is less for those systems in which (a) the free-energy curve for the intermetallic compound is sharper and deeper, (b) the liquid solubility is more limited, and (c) the proportion of component A in the intermetallic compound is greater.

Using the approximation for the tangent line,

$$\Delta\bar{F}_{A(s)} = \frac{\Delta F^f(A_xB_{1-x})}{x}. \quad (27)$$

The Σ -function then becomes

$$\Sigma = R \ln N_{A(l)} = \frac{\Delta F_A^m}{T} - \frac{\Delta F^f(A_xB_{1-x})}{xT}. \quad (28)$$

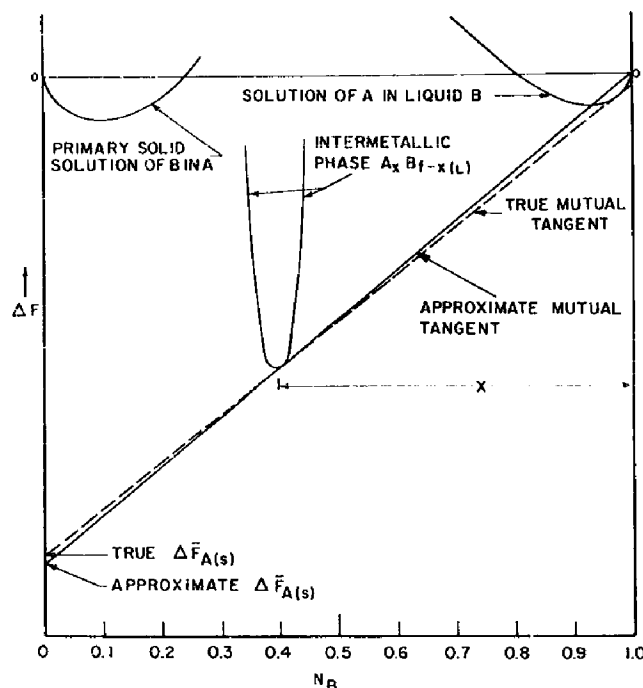


Fig. 4 - Free-energy diagram for a system A-B containing an intermetallic compound $A_x B_{1-x}$ in equilibrium with a B-rich liquid

Note that any phase transformations in the intermetallic compound are properly dealt with through the use of the free-energy-function method for the calculation of $\Delta F^f(A_x B_{1-x})$.

EVALUATION OF THE CONSTANTS IN $\log s = C/T + D$

A common expression employed to fit solubility results is

$$\log s = \frac{C}{T} + D \quad (29)$$

where the solubility s may be expressed in a variety of units and C and D are assumed to be constants. C corresponds to the temperature coefficient of solubility employed in earlier correlation studies (2,3). It is of considerable interest to evaluate C and D in terms of the thermodynamic solution parameters $\Delta \bar{H}_{A(l)}^\infty$ and $\Delta \bar{S}_{A(l)}^{xs,\infty}$ appearing in the Σ -function treatment, cf. Eq. (21). For this purpose, Eq. (29) is rewritten as

$$\log s = \frac{\ln(k N_{A(l)})}{\ln 10} = \frac{C}{T} + D \quad (30)$$

where k is the ratio of the solubility s , in whatever units have been used, to the atom-fraction $N_{A(l)}$; i.e.,

$$k = \frac{s}{N_{A(l)}} \quad (31)$$

Thus,

$$\ln N_{A(l)} = \frac{2.303C}{T} + 2.303D - \ln k \quad (32)$$

To establish a parallel relation from the Σ -function treatment, ΔF_A^m and $\Delta \bar{F}_{A(s)}$ are first written explicitly as

$$\Delta F_A^m = \Delta H_A^m - T \Delta S_A^m, \quad (33)$$

$$\Delta \bar{F}_{A(s)} = \Delta \bar{H}_{A(s)} + RT \ell_n N_{A(s)} - T \Delta \bar{S}_{A(s)}^{xs}, \quad (34)$$

Equation (21) may now be written as

$$\begin{aligned} \Sigma &= R \ell_n N_{A(\ell)} + \frac{\Delta H_A^m}{T} - \Delta S_A^m - \frac{\Delta \bar{H}_{A(s)}}{T} - R \ell_n N_{A(s)} + \Delta \bar{S}_{A(s)}^{xs} \\ &= (1 - N_{A(\ell)})^2 \left[-\frac{\Delta \bar{H}_{A(\ell)}^\infty}{T} + \Delta \bar{S}_{A(\ell)}^{xs, \infty} \right]. \end{aligned} \quad (35)$$

Rearranging,

$$\begin{aligned} \ell_n N_{A(\ell)} &= -\frac{(1 - N_{A(\ell)})^2 \Delta \bar{H}_{A(\ell)}^\infty + \Delta H_A^m - \Delta \bar{H}_{A(s)}}{RT} \\ &\quad + \frac{(1 - N_{A(\ell)})^2 \Delta \bar{S}_{A(\ell)}^{xs, \infty} + \Delta S_A^m - \Delta \bar{S}_{A(s)}^{xs}}{R} + \ell_n N_{A(s)}. \end{aligned} \quad (36)$$

Restricting attention to dilute solutions, the terms C and D may be identified by comparison of Eqs. (32) and (36); thus,

$$C = -\frac{\Delta \bar{H}_{A(\ell)}^\infty + \Delta H_A^m - \Delta \bar{H}_{A(s)}}{2.303 R}, \quad (37)$$

$$D = \frac{\Delta \bar{S}_{A(\ell)}^{xs, \infty} + \Delta S_A^m - \Delta \bar{S}_{A(s)}^{xs}}{2.303 R} + \log (k N_{A(s)}). \quad (38)$$

These expressions for C and D are rigorously correct only when the various terms in ΔH , ΔS , and $N_{A(s)}$ are independent of temperature. In many cases these terms vary relatively slowly with temperature so that, for dilute solutions, it is often possible to apply Eqs. (33) and (38) to obtain approximate values of $\Delta \bar{H}_{A(\ell)}^\infty$ and $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$ from a plot of $\log s$ versus $1/T$. However, such plots should show abrupt changes in the slope and intercept at temperatures of transition or with other changes in the nature of the A-rich phase. These changes in slope and intercept are proportional, respectively, to the enthalpy and entropy changes of component A in the A-rich phase.

THE THERMODYNAMIC CONDITIONS FOR LOW SOLUBILITY

In view of the unusual behavior of several systems for which the solvent-to-solute radius ratio is large (2,3), it is of interest to examine Eq. (36) to see what values of $\Delta \bar{H}_{A(\ell)}^\infty$ and $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$ correspond to very low solubilities. Ignoring the correction term for solubility in the A-rich phase (unimportant in the systems for which the unusual behavior has been observed), Eq. (36) may be expressed for dilute solutions as

$$\ell_n N_{A(\ell)} = -\frac{\Delta \bar{H}_{A(\ell)}^\infty + \Delta H_A^m}{RT} + \frac{\Delta \bar{S}_{A(\ell)}^{xs, \infty} + \Delta S_A^m}{R}. \quad (39)$$

A general rule for the estimation of the entropy of fusion of metals is given by Kubaschewski and Evans (16) as

$$\Delta S_{A, T_A^m}^m = 2.2 \text{ cal } ^\circ\text{K}^{-1} \text{ gm-atom}^{-1}. \quad (40)$$

Thus,

$$\Delta H_{A, T_A^m}^m = 2.2 T_A^m \text{ cal gm-atom}^{-1}. \quad (41)$$

Applying these approximate relations to Eq. (39),

$$\ln N_{A(\ell)} = - \frac{\Delta \bar{H}_{A(\ell)}^\infty}{RT} + \frac{\Delta \bar{S}_{A(\ell)}^{xs, \infty}}{R} - \frac{2.2}{R} \left(\frac{T_A^m}{T} - 1 \right). \quad (42)$$

The last term represents the solubility in a system in which the liquid solution displays ideal behavior. Thus, the temperature coefficient of solubility for a system obeying Raoult's law and whose solute follows the rule expressed by Eq. (37) is given by

$$\frac{d(R \ln N_{A(\ell)})}{d(1/T)} = -2.2 T_A^m. \quad (43)$$

For liquid alloys in which the solute atoms occupy substitutional sites in the liquid structure, the entropy of formation is expected to be near that calculated for ideal solutions. In such cases, which appear to comprise the majority of liquid metal solutions, $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$ is small (10,16,17). For these systems Eq. (42) shows that very low solubilities obtain only when $\Delta \bar{H}_{A(\ell)}^\infty$ is large and positive. Thus a very low solubility is ordinarily accompanied by a high temperature coefficient. For example, if $\Delta \bar{S}_{A(\ell)}^{xs, \infty} = 0$ and $T_A^m = 1500^\circ\text{K}$, a solubility of $N_{A(\ell)} = 10^{-5}$ at $T = 1000^\circ\text{K}$ corresponds to a value of $\Delta \bar{H}_{A(\ell)}^\infty$ near 22 kcal gm-atom⁻¹.

In the systems demonstrating unusual behavior, e.g., Fe or Ni in liquid Na (2), very low solubilities are found, together with low temperature coefficients. In such cases $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$ has a large negative value. Thus, if $\Delta \bar{H}_{A(\ell)}^\infty = 5 \text{ kcal gm-atom}^{-1}$ and $T_A^m = 1500^\circ\text{K}$, a solubility of $N_{A(\ell)} = 10^{-5}$ at 1000°K corresponds to a value of $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$ near $-17 \text{ cal } ^\circ\text{K}^{-1} \text{ gm-atom}^{-1}$. Such deviations from ideal substitutional behavior are too large to be attributed to thermal contributions, which would involve very large deviations from the Kopp-Neumann rule. In terms of configurational contributions, the most elementary explanation for large negative values of $\Delta \bar{S}_{A(\ell)}^{xs, \infty}$ is that the number of favorable sites for solute atoms in the solvent matrix is much smaller than the total number of either substitutional or interstitial sites.

EXAMPLES OF THE APPLICATION OF THE Σ-FUNCTION TREATMENT

This report is concluded by the presentation of some examples of the use of the Σ-function method for the treatment of solubility data reported in the literature for several binary liquid-metal systems. The treatment is given in some detail for the first system, Mg-Fe; for the other systems only the essential features are indicated. For brevity, all numerical values of thermodynamic quantities are expressed in terms of the absolute calorie, the gram-atom, and the Kelvin degree. Thus, the units of C_p and ΔS are cal $^\circ\text{K}^{-1} \text{ gm-atom}^{-1}$, and those of ΔH and ΔF are cal gm-atom⁻¹.

Magnesium-Iron

The solubility of solid iron in liquid magnesium is slight. The solid phases in equilibrium with the liquid solution are essentially pure Fe (18). Over the temperature range for which solubility data are available, Fe undergoes two solid-state transitions, viz., the α - γ transition at 1183°K and the magnetic transition occurring in the neighborhood of 1033°K (10). Several good sets of solubility determinations are available (19-21). In each case the solubility was determined by wet chemical analysis of samples which had been held at controlled temperatures for periods long enough to ensure saturation of the liquid Mg.

In evaluating the Σ -function it is first noted that the highest solubility reported is 0.84 weight-percent Fe, which corresponds to $N_{\text{Fe}(\ell)} = 0.0037$. The correction for concentrated solutions is thus small but not neglected in the following treatment of the data. Since the solubility of Mg in solid Fe is negligible, $\Delta\bar{F}_{\text{Fe}(s)}$ is zero, and the Σ -function reduces to

$$\Sigma(\text{Fe in Mg}, \ell) = R \ln N_{\text{Fe}(\ell)} + \frac{\Delta F_{\text{Fe}}^m}{T} \quad (44)$$

The term $\Delta F_{\text{Fe}}^m/T$ is evaluated by means of Eq. (12). The free-energy function for $\text{Fe}(\ell)$ is constructed by extrapolation of data at higher temperatures using the heat capacity expression,

$$C_{p, \text{Fe}(\ell)} = 9.72 + 0.43 \times 10^{-3} T \quad (45)$$

Thus, applying Eq. (11),

$$\left(\frac{F_T - H_{st}}{T} \right)_{\text{Fe}(\ell)} = - \frac{636}{T} - 22.381 \log T - 0.215 \times 10^{-3} T + 59.382, \quad (46)$$

where st is 298.15°K. Values of $(F_T - H_{st}/T)_{\text{Fe}(s)}$ are obtained from tables (10); the phase transitions in solid Fe prevent the development of a simple analytic expression similar to Eq. (45). The values of $\Delta F_{\text{Fe}}^m/T$ calculated by Eq. (12) are plotted in Fig. 5. The changes in slope at the transition temperatures are barely discernible owing to the small enthalpy changes accompanying these transitions (e.g., $\Delta H_{1183^\circ\text{K}}^{\alpha-\beta} = 215$ (13) and $\Delta H_{1033^\circ\text{K}}^{\text{magnetic}} = 410$ (14)). Values of $\Delta F_{\text{Fe}}^m/T$ calculated from Eq. (8), on the assumption that ΔC_p is negligible, are included in Fig. 5 to show the difference from the values calculated by the more exact free-energy-function method. At temperatures near the melting point of Fe (1812°K) the differences are negligible, but at lower temperatures the differences become important, e.g., 0.2 cal °K⁻¹ gm-atom⁻¹ at 1000°K.

The solubility results in the literature have been reported in units of weight-percent of Fe. The evaluation of Σ for each datum point can be expedited by noting that for dilute solutions

$$N_{\text{Fe}(\ell)} = W_{\text{Fe}(\ell)} \frac{M_{\text{Mg}}}{M_{\text{Fe}}} = W_{\text{Fe}(\ell)} \frac{24.32}{55.85}, \quad (47)$$

where $W_{\text{Fe}(\ell)}$ is the weight-percent of Fe in $\text{Mg}(\ell)$, and M_{Mg} and M_{Fe} are the atomic weights of Mg and Fe. Using Eq. (47),

$$\Sigma(\text{Fe in Mg}, \ell) = 4.576 \log W_{\text{Fe}} - 1.652 + \frac{\Delta F_{\text{Fe}}^m}{T} \quad (48)$$

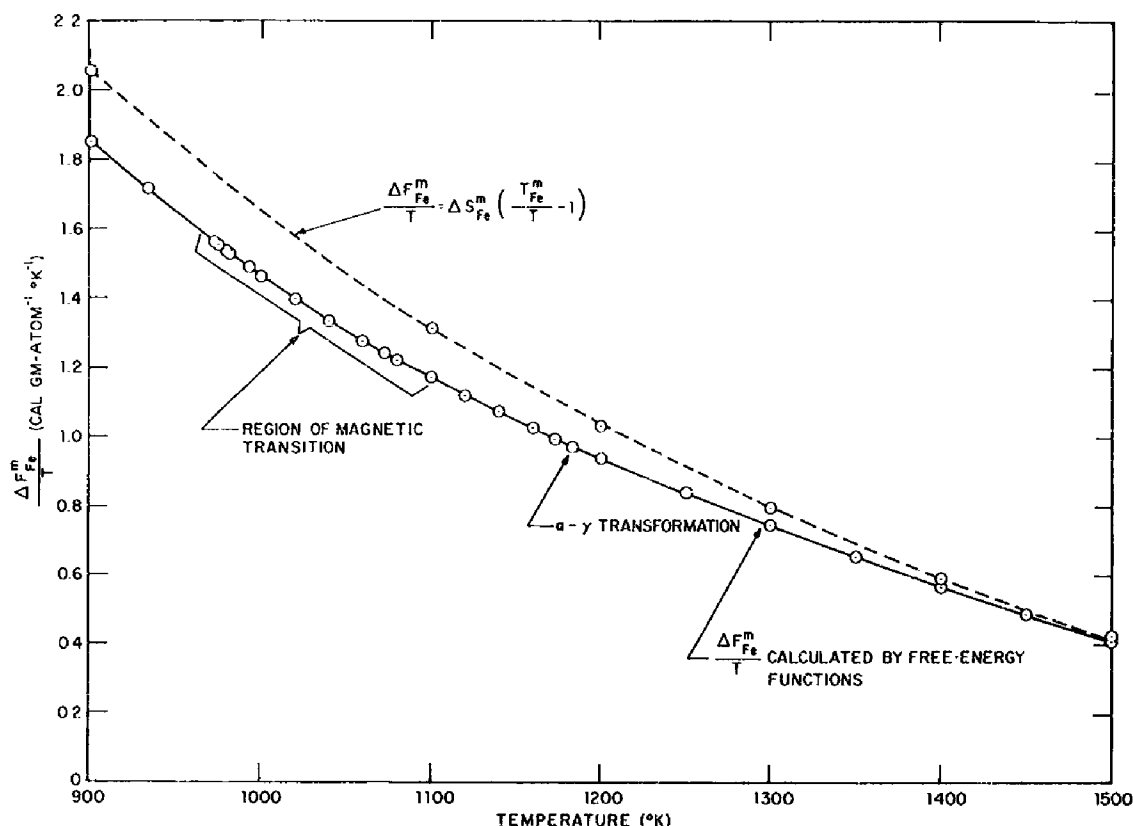


Fig. 5 - The term $\Delta F_{Fe}^m/T$ of the Σ -function for Fe(s). The upper curve is obtained by use of Eq. (8) on the assumption that ΔC_p is negligible. The lower curve, calculated by means of the free-energy functions for solid and liquid Fe, is more exact and takes account of the transitions in Fe(s) at 1183°K and near 1033°K.

Values of $\Sigma'(\text{Fe in Mg}, \ell) = \Sigma(\text{Fe in Mg}, \ell)/(1 - N_{Fe}(\ell))^2$, calculated from the results of Mitchell (19), Fahrenhorst and Bulian (20), and Siebel (21), are plotted in Fig. 6 as a function of $1/T$. These data are replotted on a reduced scale in Fig. 7 to show the intercept at $1/T = 0$ of the best straight line fitted to the data. The values of $\Delta \bar{H}_{Fe}(\ell)$ and $\Delta \bar{S}_{Fe}^{xs, \infty}(\ell)$ obtained for each set of data are given in Table 1. The Σ -function plot is well suited for the estimation of the uncertainties in $\Delta \bar{H}_{Fe}(\ell)$ and $\Delta \bar{S}_{Fe}^{xs, \infty}(\ell)$, which are also given in Table 1. The data have also been treated by plotting $\log W_{Fe}$ versus $1/T$, where W_{Fe} is the weight-percent of Fe in liquid Mg, and the results for $\Delta \bar{H}_{Fe}(\ell)$ and $\Delta \bar{S}_{Fe}^{xs, \infty}(\ell)$ are also given in Table 1. In this case the two methods give similar results owing to the fact that all data refer to dilute solutions; however, the Σ -function method was found to be more satisfactory in estimating the uncertainties in $\Delta \bar{H}_{Fe}(\ell)$ and $\Delta \bar{S}_{Fe}^{xs, \infty}(\ell)$.

Weighted-mean values for $\Delta \bar{H}_{Fe}(\ell)$ and $\Delta \bar{S}_{Fe}^{xs, \infty}(\ell)$, as obtained by the Σ -function method, have been selected as follows:

$$\Delta \bar{H}_{Fe}(\ell) = 13,700 \pm 600,$$

$$\Delta \bar{S}_{Fe}^{xs, \infty}(\ell) = -1.5 \pm 0.6.$$

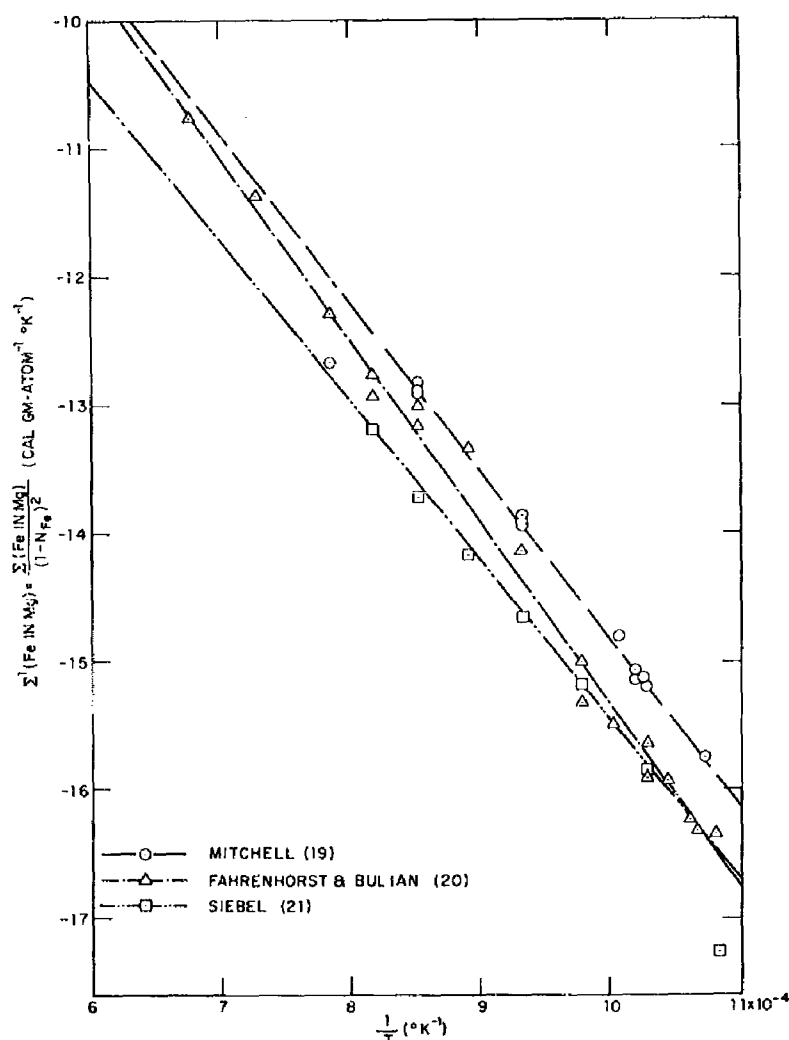


Fig. 6 - Values of $\Sigma'(\text{Fe in Mg}, \ell)$ calculated from solubility data reported in the literature

Lead-Nickel

The solubility of Pb in solid Ni is believed to be slight (1.2 atomic percent or less (18) and is therefore neglected in calculating $\Sigma(\text{Ni in Pb})$. However, the solubility of Ni in liquid Pb is large, and measurements have been reported at solubilities as high as $N_{\text{Ni}} = 0.24$. Since the eutectic, i.e., the point of minimum solubility, lies at $N_{\text{Ni}} = 0.003$, the Σ -function as modified for extension to moderately concentrated solutions is required cf. Eq. (21).

Two sets of solubility data (22,23) are available for treatment, and values of $\Sigma'(\text{Ni in Pb}, \ell)$ are plotted in Fig. 8. The data of Alden, Stevenson, and Wulff (23) are given the greatest weight in evaluating the thermodynamic parameters:

$$\Delta \bar{H}_{\text{Ni}(\ell)}^{\infty} = 3050 \pm 600 .$$

$$\Delta \bar{S}_{\text{Ni}(\ell)}^{\text{xs}, \infty} = -2.30 \pm 0.6 .$$

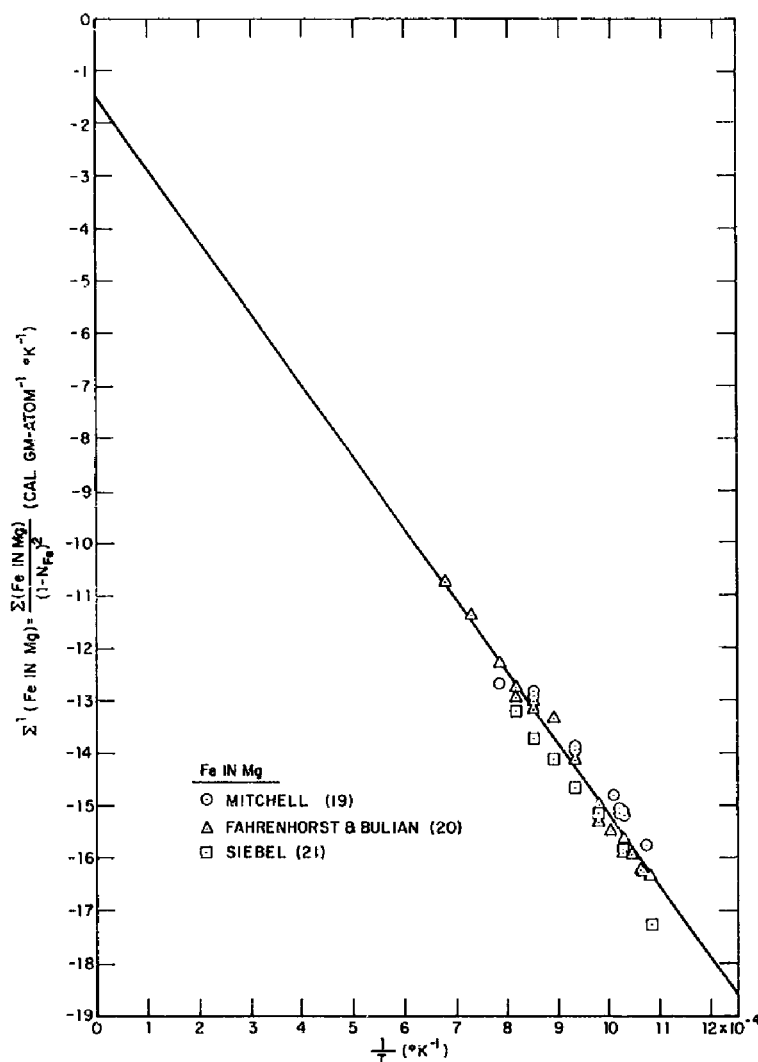


Fig. 7 - The Σ' -function values of Fig. 6 plotted on a reduced scale to show the intercept at $1/T = 0$. $\Delta \bar{H}_{Fe(l)}^{\infty} = 13,700 \pm 600$; $\Delta \bar{S}_{Fe(l)}^{xs, \infty} = -1.5 \pm 0.6$.

Table 1
Values of $\Delta \bar{H}_{Fe(l)}^{\infty}$ and $\Delta \bar{S}_{Fe(l)}^{xs, \infty}$ for Mg-Fe

$\Delta \bar{H}_{Fe(l)}^{\infty}$ (cal gm-atom ⁻¹)		$\Delta \bar{S}_{Fe(l)}^{xs, \infty}$ (cal °K ⁻¹ gm-atom ⁻¹)		Ref.
Data Treatment by Σ -Function	Data Treatment by $\log W_{Fe} = C/T + D$	Data Treatment by Σ -Function	Data Treatment by $\log W_{Fe} = C/T + D$	
13,200 ± 800	13,400	-1.6 ± 0.7	-1.5	19
14,200 ± 700	14,200	-1.1 ± 0.6	-1.2	20
12,600 ± 2000	12,900	-2.9 ± 2.0	-2.6	21

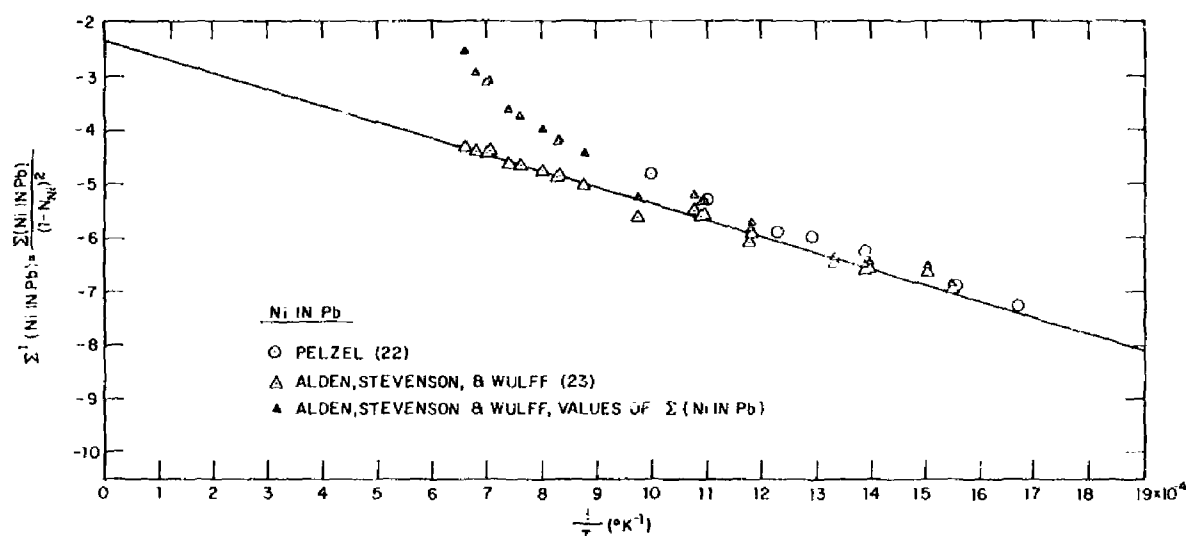


Fig. 8 - The Σ -function treatment of data for the solubility of Ni in liquid Pb.

$$\Delta \bar{H}_{\text{Ni}(\ell)}^{\infty} = 3050 \pm 600; \Delta \bar{S}_{\text{Ni}(\ell)}^{xs, \infty} = -2.30 \pm 0.6.$$

Values of $\Sigma(\text{Ni in Pb}, \ell)$, not divided by the subregular solution factor $(1 - N_{\text{Ni}})^2$, are indicated in Fig. 8 for the data of Alden et al. to show the value of the modified Σ' -function for the treatment of moderately concentrated solutions. In this case $\Sigma'(\text{Ni in Pb}, \ell)$ is linear as far as the solubility data extend, i.e., to $N_{\text{Ni}} = 0.24$.

Bismuth-Beryllium

Measurements of the solubility of Be in liquid Bi have recently been reported by Horsley and Maskrey (24). These workers found no evidence for the existence of inter-metallic compounds; the values of $\Sigma(\text{Be in Bi}, \ell)$ have, therefore, been calculated assuming that the solid phase is pure Be. The values of $\Delta F_{\text{Be}}^m/T$ were constructed from the data and estimates reported by Stull and Sinke (14); a value of $C_{p, \text{Be}(\ell)} = 7.5$ was used. The values of the thermodynamic parameters evaluated from the data shown in Fig. 9 are

$$\Delta \bar{H}_{\text{Be}(\ell)}^{\infty} = 22,400 \pm 4000,$$

$$\Delta \bar{S}_{\text{Be}(\ell)}^{xs, \infty} = 5.9 \pm 2.5.$$

Lead-Zinc

The Pb-Zn system is of special interest since the metals display immiscibility in the liquid state as well as the solid state (18). Extensive data are available for both the lead-rich and the zinc-rich solubility equilibria, and at least two attempts have been made to develop a self-consistent set of thermodynamic relations through detailed evaluation of all thermodynamic and phase data available for the system (10,25).

The approach employed here in applying the Σ -function treatment to the Pb-Zn equilibrium data is based on the method of successive approximations since, in principle, the thermodynamic results for the solute phase are necessary in order to evaluate rigorously the data for the solvent phase. The data for the phase of more extensive solubility, i.e., the Pb-rich phase, are evaluated first since the approximations necessary in evaluating

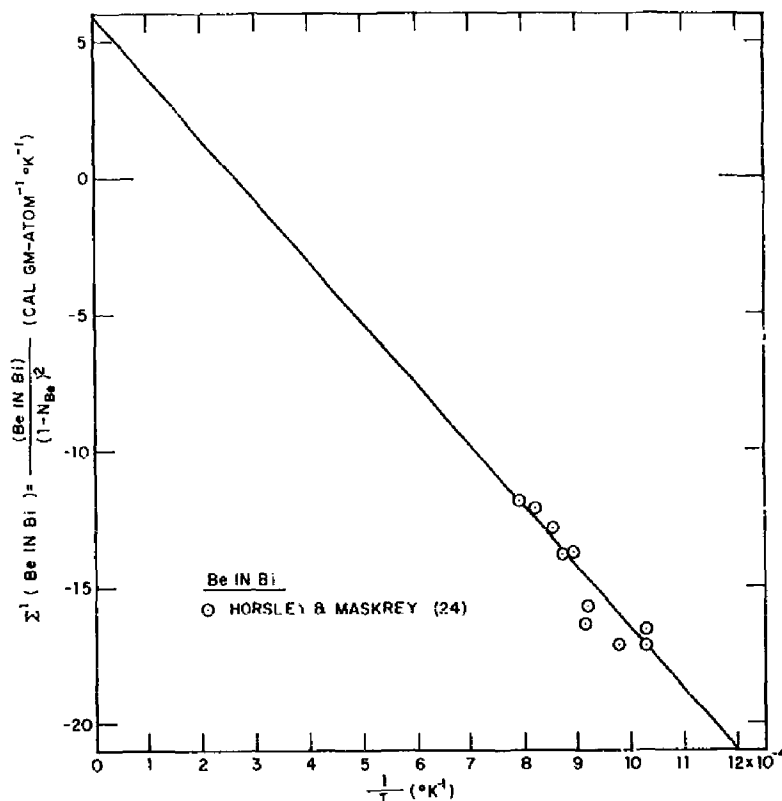


Fig. 9 - The Σ -function treatment of data for the solubility of Be in liquid Bi. $\Delta\bar{H}_{\text{Be}(\ell)}^{\infty} = 22,400 \pm 4000$; $\Delta\bar{S}_{\text{Be}(\ell)}^{\text{xs},\infty} = 5.9 \pm 2.5$.

the Σ -functions are less extensive. On the basis of the values of $\Delta\bar{H}_{\text{Zn}(\text{Pb},\ell)}^{\infty}$ and $\Delta\bar{S}_{\text{Zn}(\text{Pb},\ell)}^{\text{xs},\infty}$ derived for the Pb-rich phase, the Σ -functions for the Zn-rich phase are computed, and the corresponding values of $\Delta\bar{H}_{\text{Pb}(\text{Zn},\ell)}$ and $\Delta\bar{S}_{\text{Pb}(\text{Zn},\ell)}$ are evaluated. A second series of evaluations can then be performed if the data warrant it.

Σ -functions for the Pb-rich phase have been calculated from the equilibrium data of Waring, Anderson, Springer, and Wilcox (26), Kleppa (27), and Hass and Jellinek (28), and the results in terms of $\Sigma'(\text{Zn in Pb},\ell)$ are plotted in Fig. 10. The form of the Σ' -function is

$$\Sigma'(\text{Zn in Pb},\ell) = \frac{1}{2 N_{\text{Pb}(\text{Pb},\ell)}} \left[R \ln \left(\frac{N_{\text{Zn}(\text{Pb},\ell)}}{N_{\text{Zn}(\text{Zn},\ell)}} \right) + \frac{\Delta F_{\text{Zn}}^m}{T} \right] \quad (49)$$

where $N_{\text{Zn}(\text{Zn},\ell)} = 1$ below $T_{\text{Zn}}^m = 692.6^\circ\text{K}$ and $\Delta F_{\text{Zn}}^m = 0$ above T_{Zn}^m . The data of Springer and Romanoff (29) are inordinately high and were not used. Lumsden has evaluated the eutectic point from the experimental results of Hodge and Heyer (30) and Heycock and Neville (31), and the Σ' -functions are also shown in Fig. 10.

The values of the thermodynamic parameters corresponding to the line shown in Fig. 10 are

$$\Delta\bar{H}_{\text{Zn}(\text{Pb},\ell)}^{\infty} = 4400 \pm 800$$

$$\Delta\bar{S}_{\text{Zn}(\text{Pb},\ell)}^{\text{xs},\infty} = -0.1 \pm 1.0.$$

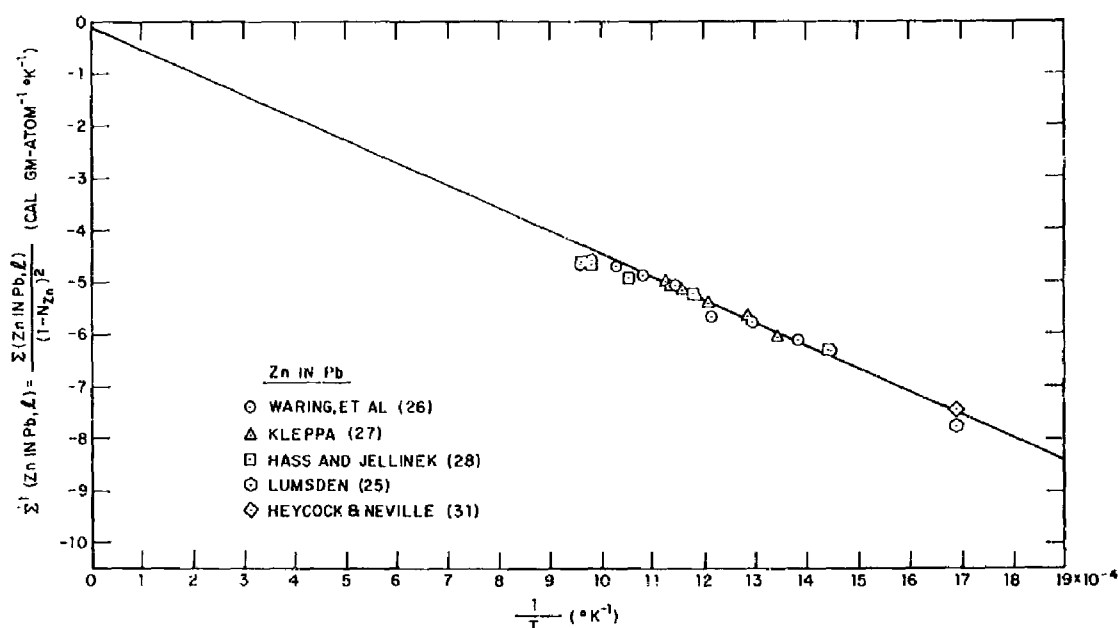


Fig. 10 - The Σ' -function treatment of data for the solubility of Zn in liquid Pb.

$$\Delta \bar{H}_{\text{Zn(Pb, l)}}^{\infty} = 4400 \pm 800; \Delta \bar{S}_{\text{Zn(Pb, l)}}^{\text{xs}, \infty} = -0.1 \pm 1.0.$$

The form of the Σ' -function for the Zn-rich phase is

$$\Sigma'(\text{Pb in Zn, l}) = \frac{1}{N_{\text{Zn}}^2(\text{Zn, l})} \left[R \ln \left(\frac{N_{\text{Pb}}(\text{Zn, l})}{N_{\text{Pb}}(\text{Pb, l})} \right) - \frac{N_{\text{Zn}}^2(\text{Pb, l})}{T} \frac{a_{\text{Zn}}^{\infty}(\text{Pb, l})}{T} \right] \quad (50)$$

where $a_{\text{Zn}}^{\infty}(\text{Pb, l})$ is the subregular solution parameter representing the deviation from ideal solution behavior; $a_{\text{Zn}}^{\infty}(\text{Pb, l})$ is given by

$$a_{\text{Zn}}^{\infty}(\text{Pb, l}) = \Delta \bar{F}_{\text{Zn(Pb, l)}}^{\text{xs}, \infty} = \Delta \bar{H}_{\text{Zn(Pb, l)}}^{\infty} - T \Delta \bar{S}_{\text{Zn(Pb, l)}}^{\text{xs}, \infty} \quad (51)$$

In view of the fact that $\Delta \bar{S}_{\text{Zn(Pb, l)}}^{\text{xs}, \infty}$ is nearly zero, the calculations can be simplified by assuming that $a_{\text{Zn}}^{\infty}(\text{Pb, l})$ is temperature independent; the value of $a_{\text{Zn}}^{\infty}(\text{Pb, l})$ was therefore assumed to be 4450.

Values of the Σ' -functions calculated from the data of Waring, Anderson, Springer, and Wilcox (26), Kleppa (27), Hess and Jellinek (28), Lumsden (25), Heycock and Neville (31), and Spring and Romanoff (29) are plotted in Fig. 11. The thermodynamic parameters corresponding to the straight line placed through the data are

$$\Delta \bar{H}_{\text{Pb(Zn, l)}}^{\infty} = 12,900 \pm 1300$$

$$\Delta \bar{S}_{\text{Pb(Zn, l)}}^{\text{xs}, \infty} = 7.0 \pm 2.0.$$

The scatter of the data of Figs. 10 and 11 indicate that little improvement is to be expected through another series of evaluations based on the data derived above. If a second series were to be undertaken it would be desirable to employ the subregular solution equations (5) to express the functional dependencies of the entropies and heats of solution on the temperature and the composition.

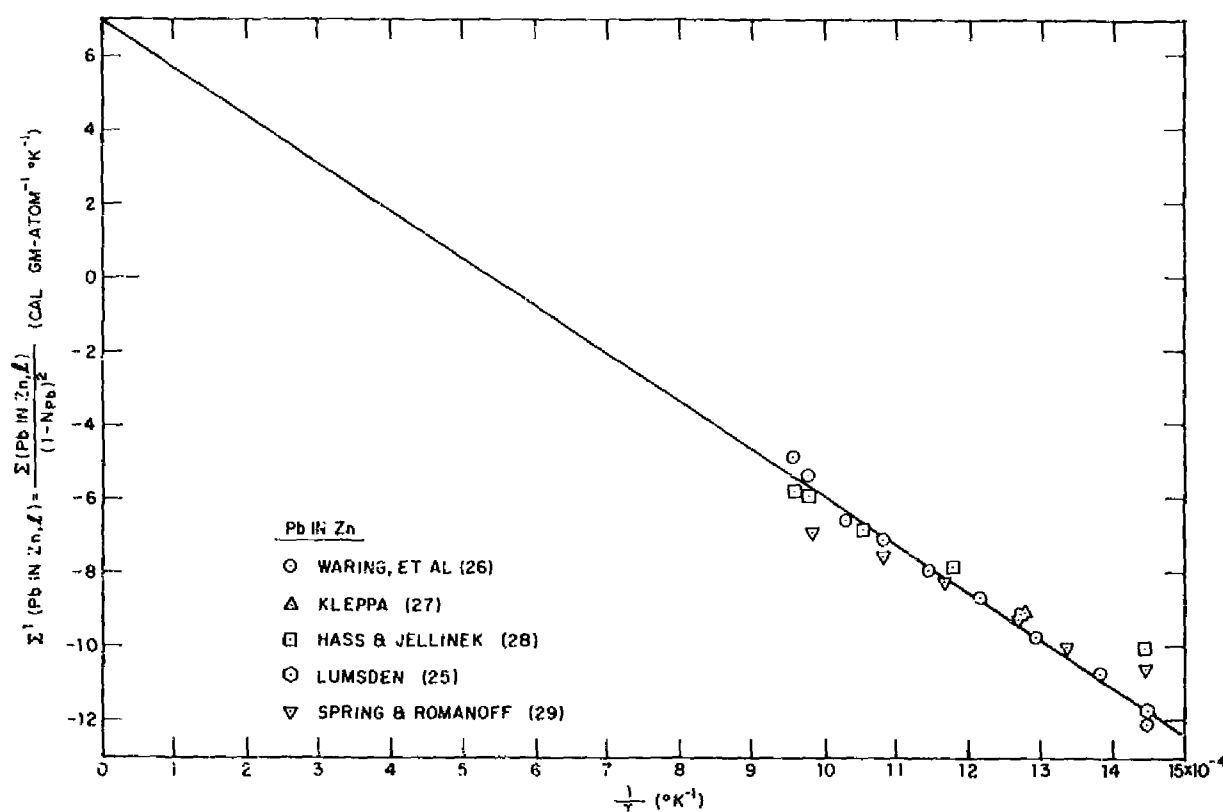


Fig. 11 - The Σ -function treatment of the data for the solubility of Pb in liquid Zn.

$$\Delta \bar{H}_{\text{Pb}(\text{Zn}, \ell)}^{\infty} = 12,900 \pm 1300; \Delta \bar{S}_{\text{Pb}(\text{Zn}, \ell)}^{\text{xs}, \infty} = 7.0 \pm 2.0.$$

Lead-Copper

The solubility of Pb in solid Cu is low and is neglected in calculating values of $\Sigma'(\text{Cu in Pb}, \ell)$. Excellent data are available for a wide range of temperatures and extend to solubilities as high as $N_{\text{Cu}} = 0.25$. The data of Kleppa and Weil (8), Pelzel (32), and Heycock and Neville (33) are plotted in Fig. 12. An excellent straight line is defined by the data of Kleppa and Weil, and of Heycock and Neville; this line corresponds to

$$\Delta \bar{H}_{\text{Cu}(\ell)}^{\infty} = 6900 \pm 400$$

$$\Delta \bar{S}_{\text{Cu}(\ell)}^{\text{xs}, \infty} = 1.6 \pm 0.4.$$

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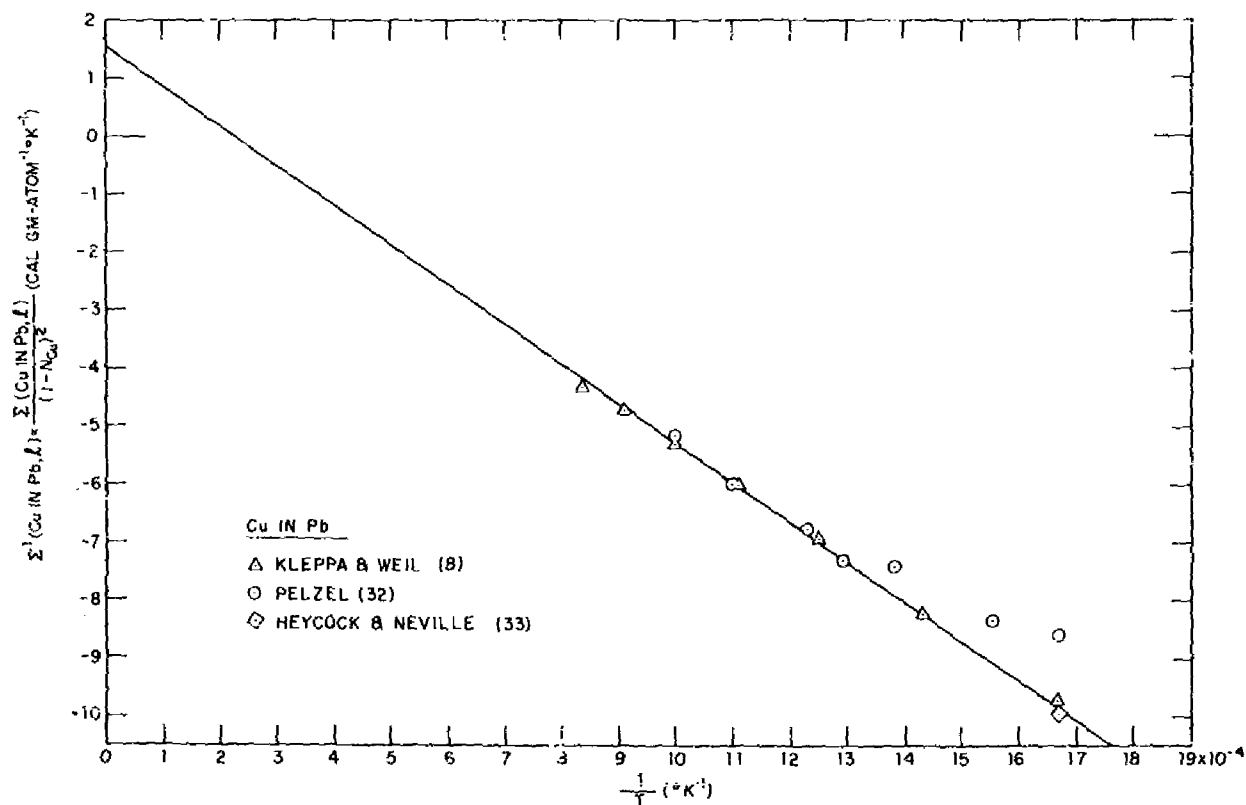


Fig. 12 - The Σ -function treatment of data for the solubility of Cu in liquid Pb.

$$\Delta \bar{H}_{\text{Cu}(\ell)}^{\infty} = 6900 \pm 400; \Delta \bar{S}_{\text{Cu}(\ell)}^{\text{xs}, \infty} = 1.6 \pm 0.4.$$

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<p>UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 5555. A THERMODYNAMIC ANALYSIS OF SOLUBILITY IN LIQUID METAL SYSTEMS by J. L. White. 22 pp. & figs., December 7, 1960.</p> <p>Binary liquid-metal solubility equilibria of the type A (in solid or liquid phase) \rightleftharpoons A (in liquid B) are analyzed in terms of the fundamental thermodynamic solution parameters ΔH_A^{ex} and ΔS_A^{ex}, the heat and entropy, respectively, of solution of the liquid solute at infinite dilution in the liquid solvent. A general method for the treatment of equilibrium solubility data is developed and is termed the Σ'-function method, in view of its similarity to the standard Σ-function method for the treatment of vapor-pressure data.</p> <p>UNCLASSIFIED (Over)</p>	<p>UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 5555. A THERMODYNAMIC ANALYSIS OF SOLUBILITY IN LIQUID METAL SYSTEMS by J. L. White. 22 pp. & figs., December 7, 1960.</p> <p>Binary liquid-metal solubility equilibria of the type A (in solid or liquid phase) \rightleftharpoons A (in liquid B) are analyzed in terms of the fundamental thermodynamic solution parameters ΔH_A^{ex} and ΔS_A^{ex}, the heat and entropy, respectively, of solution of the liquid solute at infinite dilution in the liquid solvent. A general method for the treatment of equilibrium solubility data is developed and is termed the Σ'-function method, in view of its similarity to the standard Σ-function method for the treatment of vapor-pressure data.</p> <p>UNCLASSIFIED (Over)</p>	<ol style="list-style-type: none"> 1. Liquid metals - Solubilizing effects 2. Metals - Solubility - Temperature factors <p>I. White, J. L.</p>	<ol style="list-style-type: none"> 1. Liquid metals - Solubilizing effects 2. Metals - Solubility - Temperature factors <p>I. White, J. L.</p>
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